

1.75 B.M. On the basis of these results a monomeric bridged structure as shown in Figs. 1 and 2 may be proposed.

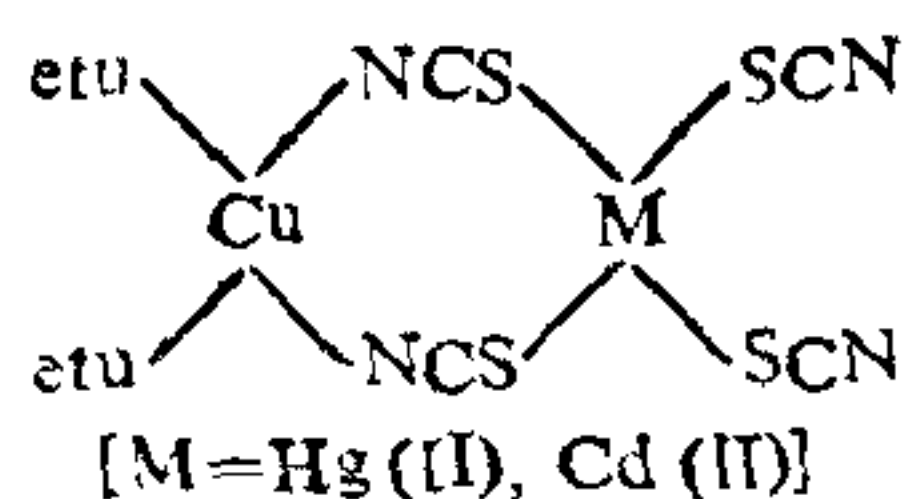


FIG. 1

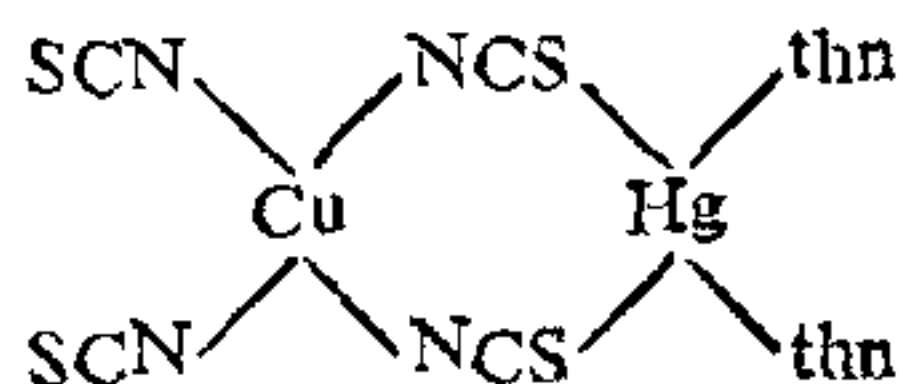


FIG. 2

Since in 'etu' 'N' is donor atom which is hard, will prefer to link with copper whereas in 'thn' in which 'S' is the donor atom which is soft will prefer to link with mercury according to HSAB theory¹⁰. If the proposed structures are true then they will belong to C_2 point group. Assuming this point group, we have calculated the infrared active modes and compared with the observed bands. This comparison again favours our proposed structures².

III. Polymeric bridged complexes: viz., (tzt)₂Cu (NCS)₂ Hg(SCN)₂.

The position and the number of infrared spectral bands due to γ CN, γ CS and δ NCS modes as presented in Table II clearly indicate the presence of only bridging thiocyanate groups in this complex^{2,3,7-9}. This complex is insoluble and decomposes at high temperatures. On the basis of these results a polymeric bridged structure in which the ligands are attached to copper may be suggested as shown in Fig. 3. Thus copper acquire distorted octahedral or tetragonal and mercury tetrahedral coordination geometry.

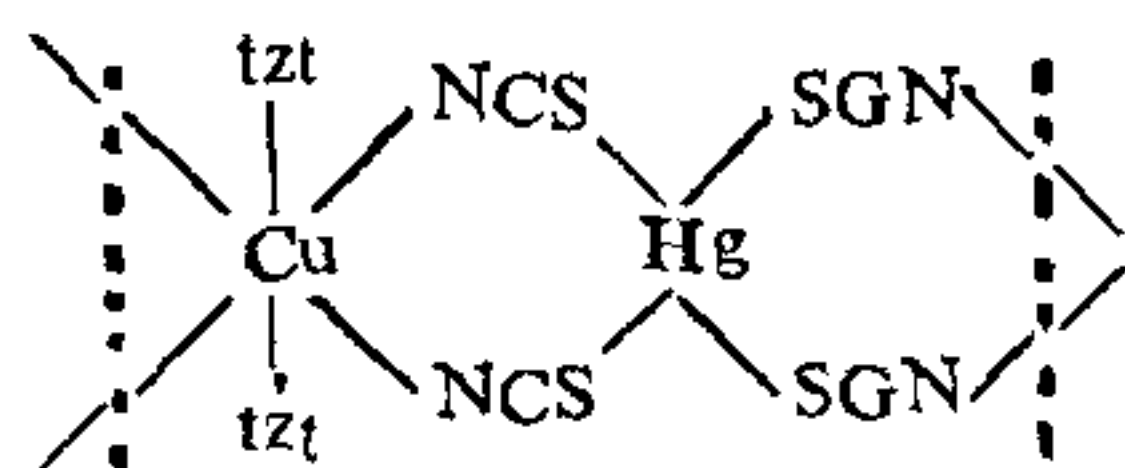


FIG. 3

This complex again belongs to C_{2v} point group for which the calculated and observed bands are compared. This comparison favours the proposed structure. The tentative assignments of γ M-NCS, γ M-L, γ Hg-SCN and γ Hg-L modes are also given in Table II in some complexes.

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HEAT OF FORMATION OF SOME ORGANIC COMPOUNDS USING IOC- ω -TECHNIQUE

HEAT of Formation of benzanthrone, acedanthrone, flavanthrone and some other organic compounds containing hetero-atoms have been calculated using IOC- ω -technique. The results obtained are in agreement with the experimental values, where ever available.

IOC- ω -technique has been widely used¹⁻⁵ to calculate the heat of formation of organic compounds. S. C. Tiwari⁶ has calculated the heat of formation of some cyclazines and some other organic compounds containing heteromolecules. The results obtained are in fairly good agreement with the available experimental results. In the present paper the method has been further used to calculate the heat of formation of benzanthrone, acedanthrone, flavanthrone and some other organic compounds containing heteromolecules.

Method of Calculation

The heat of formation of an organic compound is equal to the sum of the total π -bond and σ -bond energies (Eq. 1).

$$-\Delta H_f = E_{\pi b} + E_{\sigma b} \quad (1)$$

The π -bond energy can be obtained by using equation (2) and the principle involved in the derivation of this equation has been described in the literature¹⁻⁶:

$$E_{\pi b} = - \left[\omega \sum_r q_r (1 - q_r) - \omega_s \sum_{j < r} q_r P_{rs} + 2\beta \sum_{r > s} p_{rs} \right] \quad (2)$$

where q_r is the electronic charge at an atom r , p_{rs} is the bond-order between atom r and s and ω is an empirical parameter. Several authors⁷ have used the value of this parameter ranging from 0.33 to 1.8. In the present calculation a value 1.3 has been proposed for this parameter. The empirically adjusted parameter β has been assigned a value of 1.5. The σ bond energy ($E_{\sigma b}$) may be evaluated using Eq. (3).

$$E_{\sigma b} = N_C E_C + N_H E_H + N_X E_X \quad (3)$$

where N_C , N_H and N_X are the number of C-C, C-H and C-X bonds respectively in the given compound and X represents the hetero atom. E_C , E_H and E_X are the energies of C-C, C-H and C-X bonds. The values of the bond energies for $E_C = 4.43$, $E_H = 2.9$, $E_O = 7.7$ eV are well established. The value of $E_C = 3.7$ eV has been empirically adjusted which is very close to the value of 3.80 eV used by Devar⁹.

Result

The calculated values of the heat of formation of all the compounds using equations (1), (2) and (3) are presented in Table I. Although the experimental

TABLE I
Heat of Formation and π bond energy of some organic compounds

Compounds	π bond energy (ev)	ΔH_f (ev)	
		Cal.	Expt.
Benzanthrone	33.04	155.34	..
Acedianthrone	27.13	291.89	..
Flavanthrone	26.31	275.36	..
Melamine	5.98	55.31	..
Furan	5.59	46.79	44.98
Pyrrole	6.09	44.58	44.77
Pyridine	10.33	53.08	53.40
Porphine	37.72	187.08	..
Fulvene	9.69	62.17	..
Pyrazine	9.97	46.69	46.44
Thiazole	6.39	35.77	..

values of heat of formation of benzanthrone, acedianthrone, flavanthrone, melamine and porphine are not available, the values seem to be correct as the values of heat of formation of furan, pyrrole, pyridine, and pyrazine, calculated in the present study are in fairly good agreement with the experimental results available in all these cases.

The electronic charge and bond-order data of all the compounds have been taken from the literature¹⁰⁻¹². The results obtained clearly indicate that the simplified form of IOC- ω -technique is quite satisfactory for calculating the heats of formation of organic compounds. The fair agreement of the calculated heat of formation for a particular organic compound with the experimental results also supports the values of various parameters that have been used to calculate the electronic charge and bond-order by LCAO-MO method.

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